

## Tetrakis(2-methoxy-5-pyridyl)silane

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## Key indicators

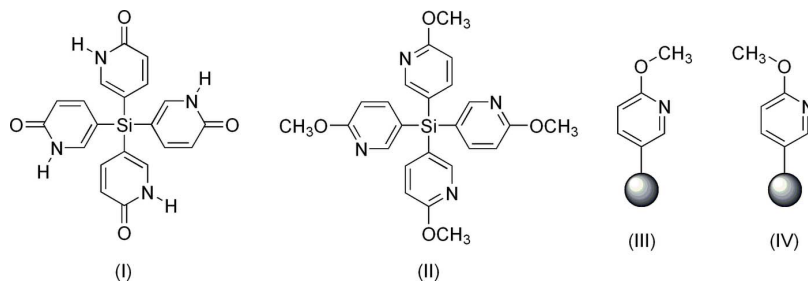
Single-crystal X-ray study  
 $T = 225$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.057  
 $wR$  factor = 0.173  
Data-to-parameter ratio = 14.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_4\text{Si}$ , crystallizes from propionic acid–hexane to produce a close-packed structure with no included guests. In contrast, crystallization of the closely related tetrakis(1,2-dihydro-2-oxo-5-pyridyl)silane under similar conditions is directed by hydrogen bonding of the pyridinone groups to yield an open diamondoid network, which is filled by a combination of interpenetration and inclusion of guests.

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## Comment

A promising strategy in crystal engineering is based on the use of molecules that can associate by forming reliable directional interactions, thereby placing their neighbors in predictable positions. Such molecules, which have been called tectons, from the Greek word for builder (Simard *et al.*, 1991), can serve as the basic elements of a rational nanoscale construction set for building crystalline networks with predetermined architectures and properties. The directional interactions that hold such structures together cannot normally be optimized when the tectons are closely packed, so the resulting networks are typically porous, with interiors filled by interpenetration of independent networks or by the inclusion of guests (Saied, Maris, Wang *et al.*, 2005; Malek, Maris, Perron & Wuest, 2005; Malek, Maris, Simard & Wuest, 2005). For example, crystallization of tetrakis(1,2-dihydro-2-oxo-5-pyridyl)silane, (I), is directed by characteristic hydrogen bonding of its pyridinone groups to give open interpenetrated diamondoid networks, in which approximately 60% of the volume remains available for the inclusion of guests (Saied *et al.*, 2003).



In contrast, the structure of the title compound, (II), is close-packed, devoid of guests, and held together primarily by a combination of van der Waals interactions, aromatic interactions,  $\text{C}-\text{H}\cdots\text{O}$  interactions, and  $\text{C}-\text{H}\cdots\text{N}$  interactions (Figs. 1 and 2). Two  $\text{C}-\text{H}\cdots\text{N}$  interactions [ $\text{H}\cdots\text{N}$  2.68 (1) Å] are formed with the closest neighbor, which is separated by an  $\text{Si}\cdots\text{Si}$  distance of 6.395 (3) Å. The average  $\text{C}-\text{Si}-\text{C}$  angle ( $109.46^\circ$ ) is very close to the ideal tetrahedral value.

As expected, the 2-methoxy-5-pyridyl groups of the title compound, (II), adopt a near-planar *syn* conformation, (III), in which the methoxy substituent lies close to the mean plane of the pyridine ring, and the methyl group is oriented toward the N atom. In this structure, the average N—C—O—C dihedral angle is 2.8°. Analysis of all 42 structures in the Cambridge Structural Database (Version 5.26 of February 2005; Allen, 2002) containing one or more 5-substituted 2-methoxy-5-pyridyl groups revealed only one example of the alternative planar *anti* conformation, (IV).

Together, our observations are a valuable addition to the growing body of evidence showing how the crystallization of tectons differs distinctively from that of close structural analogs lacking multiple sites of strong directional interaction (Saied, Maris, Simard & Wuest, 2005). Tecton (I) forms open hydrogen-bonded networks with substantial porosity, whereas its *O*-methyl derivative, (II), crystallizes under very similar conditions as a close-packed structure with no included guests. The divergent behavior of compounds (I) and (II) illustrates how suitably oriented hydrogen-bonding groups can have a profound effect as directors of crystallization.

## Experimental

Tetrakis(2-methoxy-5-pyridyl)silane, (II), was prepared from tetrakis(1,2-dihydro-2-oxo-5-pyridyl)silane, (I), by a general method for the *O*-alkylation of pyridinones (Comins & Jianhua, 1994). Crystals were grown by allowing hexane to diffuse slowly into a solution of the title compound, (II), in propionic acid.

### Crystal data

$C_{24}H_{24}N_4O_4Si$	$Z = 2$
$M_r = 460.56$	$D_x = 1.342 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 9.661 (3) \text{ \AA}$	Cell parameters from 25 reflections
$b = 10.364 (4) \text{ \AA}$	$\theta = 15.0\text{--}30.0^\circ$
$c = 12.230 (6) \text{ \AA}$	$\mu = 1.24 \text{ mm}^{-1}$
$\alpha = 107.74 (4)^\circ$	$T = 225 (2) \text{ K}$
$\beta = 94.68 (3)^\circ$	Block, colorless
$\gamma = 99.22 (3)^\circ$	$0.52 \times 0.48 \times 0.18 \text{ mm}$
$V = 1140.1 (9) \text{ \AA}^3$	

### Data collection

Enraf–Nonius CAD-4 diffractometer	3964 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{\text{int}} = 0.078$
Absorption correction: analytical (ABSORP in NRCVAX; Gabe <i>et al.</i> , 1989)	$\theta_{\text{max}} = 69.8^\circ$
$T_{\text{min}} = 0.570$ , $T_{\text{max}} = 0.810$	$h = -11 \rightarrow 11$
8614 measured reflections	$k = -12 \rightarrow 12$
4319 independent reflections	$l = -14 \rightarrow 14$
	6 standard reflections
	frequency: 60 min
	intensity decay: 0.1%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.1135P)^2 + 0.4013P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.173$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
4319 reflections	$\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$
302 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.0133 (15)

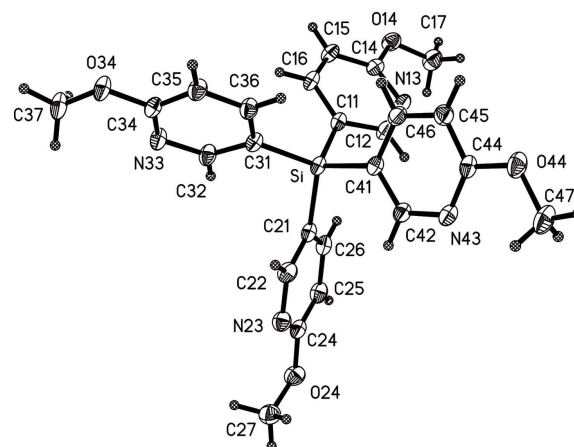


Figure 1

A view of the structure of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by spheres of arbitrary radii.

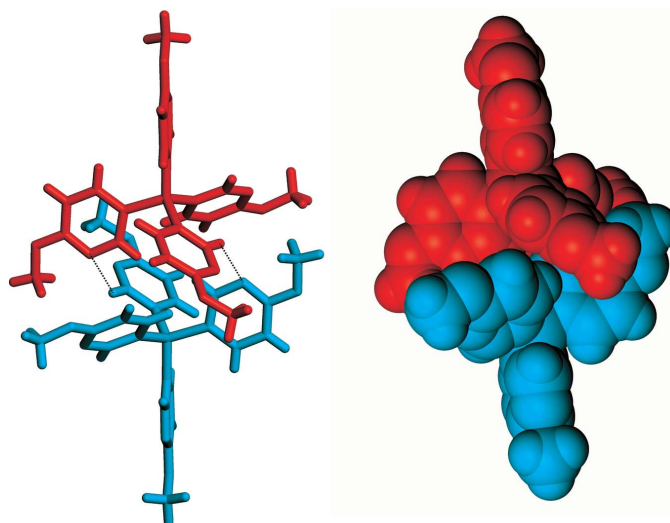


Figure 2

Views of one molecule of (II) (red) with the neighbor (light blue) that is separated from it by an Si···Si distance of 6.395 (3) Å. The two molecules illustrated are related by a center of inversion and together constitute the contents of one unit cell. The left-hand view shows the closest contacts as broken lines, with an H···N distance of 2.68 (1) Å. In the right-hand view, the molecules are shown as CPK representations.

Table 1

Selected geometric parameters (Å, °).

Si—C11	1.867 (2)	Si—C21	1.872 (2)
Si—C31	1.871 (2)	Si—C41	1.874 (2)
C11—Si—C31	110.28 (10)	C11—Si—C41	105.43 (10)
C11—Si—C21	110.38 (10)	C31—Si—C41	111.96 (10)
C31—Si—C21	109.15 (10)	C21—Si—C41	109.59 (10)
C17—O1—C14—N13	8.1 (3)	C37—O3—C34—N33	−0.6 (3)
C27—O2—C24—N23	4.3 (3)	C47—O4—C44—N43	−0.7 (3)

After confirmation of their location in a difference map, H atoms were positioned geometrically and refined using a riding model, with C—H distances in the range 0.94–0.97 Å, and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups or  $1.2U_{\text{eq}}(\text{C})$  for other atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: modified versions of *NRC-2/NRC2A* (Ahmed *et al.*, 1973); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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